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[13] The turnovers are related to the disappearance of the bisketenes **1a** – **c** and the selectivities to the formation of the dihydrofuranones **3a** – **c**. The values were obtained by IR spectroscopy after 12 h; the standard deviation is about ± 1 %. The ketenyl esters **2a** – **c** were the only observable by-products.

## Rhodium and Iridium Pyrazolato Blues**

Cristina Tejel, Miguel A. Ciriano,* José A. López, Fernando J. Lahoz, and Luis A. Oro*

Since the first report in 1908, great progress[1] has been made concerning the knowledge of the fascinating "platinum blues". These cationic complexes generally exhibit a chain of four platinum atoms of mixed valencies, and metal-metal interactions. They also show antitumor activity.[2] The tetranuclear chain is held together by an unsupported metal – metal bond between two dinuclear complexes. These invariably display a face-to-face structure bridged by two ligands of the type N-C-O (such as 2-pyridonate and related ligands; N represents an endocyclic nitrogen) in a head-to-head arrangement. This configuration contains two different platinum centers; one of which is O,O-coordinated and the other N,N-coordinated. Noticeably, the unsupported metal – metal bond is always formed between the O,O-coordinated platinum atoms, which are the less hindered centers. Interdimer bond formation between the N,N-coordinated platinum atoms has never been observed. Furthermore, as already pointed out by Matsumoto et al.,[2] the synthetic methods for some antitumor active blue compounds are not reproducible.

In contrast, related cationic compounds of the neighboring metals are rare for gold[3] and unknown for iridium. On the other hand, a range of oligomeric mixed-valence rhodium complexes has been reported,[4a] based on electronic spectroscopy solution studies, but full characterization has been carried out in only a few cases.[5] Closely related to this work is an intensely colored $[Rh_4]^{6+}$ species proposed by Gray et al.,[4b] and shown to be a mixed-valence compound by Mann et al.[5b] In all cases, the coordination planes in the metal chain are almost parallel, which is the most sterically favorable situation for the formation of oligomers. Once again, the parent species are dinuclear complexes with face-to-face arrangement or, alternatively, mononuclear compounds. Here we describe a straightforward and reproducible reaction from open-book dinuclear pyrazolato complexes, to form novel tetranuclear iridium and rhodium blue compounds.

Beautiful blue, EPR-silent solutions are obtained by mixing equimolecular amounts of the recently reported[6] yellow complexes $[\{Rh(\mu\text{-pz})(CN\textit{t}Bu)_2\}_2]$ (**1**) and $[\{Rh(\mu\text{-pz})(CN\textit{t}Bu)_2(NCMe)\}_2](PF_6)_2$ (**2**), from which crystals of the new tetranuclear "rhodium blue" complex $[\{Rh(\mu\text{-pz})(CN\textit{t}Bu)_2\}_4](PF_6)_2$ (**3**) were isolated (Figure 1; pz = pyrazolato). Alternatively, complex **3** can be obtained by oxidation of **1** with $[FeCp_2]PF_6$ (in a 1:1 molar ratio) in acetonitrile, and recrystallization of the crude solid from acetone/diethyl ether.

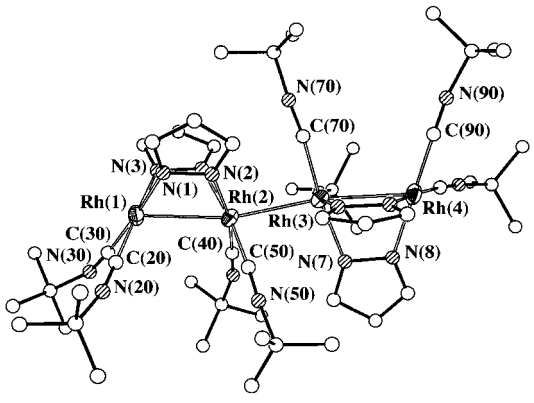


Figure 1. Molecular representation of the cation in the tetranuclear complex $[\{Rh(\mu\text{-pz})(CN\textit{t}Bu)_2\}_4](PF_6)_2$ (**3**). Only one group of atoms has been drawn for the disordered ligands. Selected bond lengths [Å] and angles [°]: Rh(1)–Rh(2) 2.721(4), Rh(2)–Rh(3) 2.713(4), Rh(3)–Rh(4) 2.723(4), Rh–N 1.99(3) – 2.13(3), Rh–C 1.84(3) – 1.97(4); Rh(1)-Rh(2)-Rh(3) 165.51(14), Rh(2)-Rh(3)-Rh(4) 167.17(15), Rh-C-N 172(3) – 179(3), C-N-C 159(4) – 176(4).

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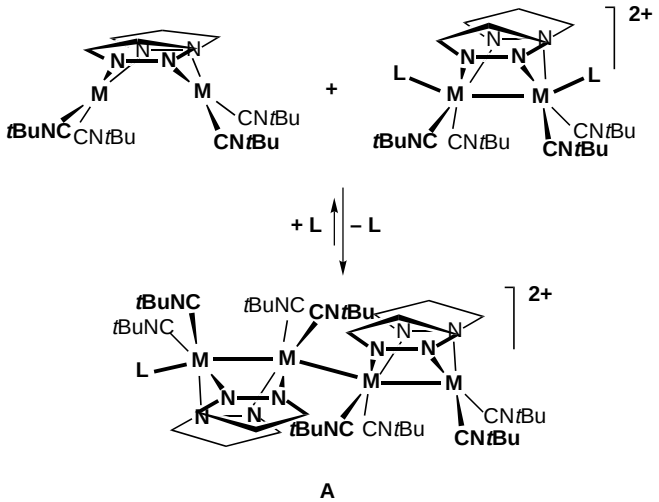
The crystal structure of **3**, determined by single-crystal X-ray diffraction, reveals tetranuclear cations together with $PF_6^-$ anions and solvent molecules.[7] Each tetranuclear complex is composed of two pyrazolato-bridged dinuclear $[(CNtBu)_2Rh(\mu\text{-}pz)_2Rh(CNtBu)_2]$ moieties linked through a nonsupported metal–metal bond (2.713(4) Å). The two dinuclear moieties show the usual boat conformation for the $Rh(\mu\text{-}pz)_2Rh$ group,[6] with dihedral angles of 49.4(9) and 48.2(8)° between the two rhodium coordination planes and Rh–Rh bond lengths of 2.721 and 2.723(4) Å. Interestingly, the two dinuclear moieties are arranged in a staggered conformation with respect to each other (N(4)-Rh(2)-Rh(3)-N(5) torsion angle 137(1)°), which allows the two metals to form the unsupported Rh(2)–Rh(3) bond. The three metal–metal bonds in the crystal structure are almost linear, with intermetallic bond angles of 165.5(2) and 167.2(2)°, analogous to those reported for the tetrameric platinum blue compounds $[(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(NH_3)_2]_2^{5+}$ (164.81 and 165.02(5)°) and $[(en)Pt(C_5H_4NO)_2Pt(en)]_2^{5+}$ (164.33(3)°)[8] (en = ethylenediamine). Moreover, the related mixed-valence cation $[Rh_2^{II}Rh^{I}(s\text{-}pqdi)_4(pqdi)_2]^+$ (s-pqdi = 9,10-phenanthrosemiquinonediimine, pqdi = 9,10-phenanthroquinonediimine) exhibits[5c] an unbridged trinuclear linear metal chain with very similar intermetallic separations (av 2.754(2) Å), although in this case, the electronic interactions between the chelating ancillary ligands lead to an eclipsed conformation of the square-planar environment of the metal atoms.

Interestingly, NMR studies show that when the rhodium(I) and rhodium(II) complexes **1** and **2** are mixed, a fast equilibrium on the NMR time scale is formed with the cationic tetranuclear species **A**, which contains an additional acetonitrile ligand coordinated at an axial position (Scheme 1). Thus, a concentrated and cold blue solution of the mixture in [D$_6$]acetone shows four signals in the $^{13}C\{^1H\}$ NMR spectrum for the C3 and C5 atoms and two signals for the C4 atom of the pyrazolate ligands, corresponding to **A**. However, a NOESY NMR spectrum indicates exchange of all the isocyanide and pyrazolate ligands, and they become equivalent in a diluted blue solution. Consequently, three averaged signals, two for the pyrazolate and one for the isocyanide ligands, are observed at room temperature in the $^1H$ NMR spectrum. The dramatic influence of the concentration on the rate of exchange supports the assumption of an intermolecular process, and the exchange agrees with the proposed chemical equilibrium (Scheme 1). In contrast to the reported cleavage of $\{[Rh(MeCN)_4](BF_4)_{1.5}\}_\infty$ into defined valence species when dissolved,[5a] it is remarkable that our tetrarhodium chain persists in the blue solutions. The formation of the unusual adduct **A** probably arises from the lability of the nitrile ligands in **2** along with the nucleophilic character of the rhodium centers in **1**. Moreover, the tetrametallic chain results from a redox-condensation reaction, so that the four metal atoms each possess a formal oxidation state of 1.5. Delocalization of the metal–metal bond through the four metal atom chain would account for the intense color. Coordination of a ligand (acetonitrile or the donor solvent) at the free axial position should break the unsupported Rh–Rh bond to regenerate the starting dinuclear complexes. Internal electron transfer in the tetrametallic chain, however, facilitated by the metal–metal bond delocalization, results in the interconversion of $[\{Rh(\mu\text{-}pz)(CNtBu)_2\}_2]$ and $[\{Rh(\mu\text{-}pz)(CNtBu)_2(NCMe)\}_2](PF_6)_2$ upon cleavage, as observed for the fluxional process.




Scheme 1. Postulated chemical equilibrium for the formation of the tetranuclear adducts **A**. L = acetonitrile, M = Rh, Ir.

Addition of iodide to the blue solutions leads to a yellow, equimolecular mixture of **1** and $[\{Rh(\mu\text{-}pz)(I)(CNtBu)_2\}_2]$, in which the tetrametallic chain is not regenerated. Therefore, at least one labile ligand *trans* to the metal-metal bond in the $Rh^{II}$ complex is required to bring about the above-mentioned condensation.

In a similar way, beautiful purple, EPR-silent solutions can be obtained by mixing the iridium complexes $[\{Ir(\mu\text{-}pz)(CNtBu)_2\}_2]$ (**4**) and $[\{Ir(\mu\text{-}pz)(CNtBu)_2(NCMe)\}_2](PF_6)_2$ (**5**). The spectroscopic properties of the blue rhodium complex and purple iridium complex in solution are similar. Thus, the $^1H$ NMR spectrum of the latter shows three averaged resonances for the pyrazolate and isocyanide ligands even at low temperature, indicative of a faster rate of exchange than for the rhodium-containing solution. In addition, the purple solutions are extremely air- and light-sensitive. In close analogy to the rhodium species, these purple solutions of the iridium complex can also be obtained by oxidation of **4** with $[FeCp_2]PF_6$ (in a 1:1 molar ratio) in acetonitrile. Oxidation of **4** with iodine (in a 1:0.5 molar ratio) yields a neutral red complex $[\{(CNtBu)_2(I)Ir(\mu\text{-}pz)_2Ir(CNtBu)_2\}_2]$ (**6**) which contains a tetrairidium chain, similar to that found for $[\{Rh(\mu\text{-}pz)(CNtBu)_2\}_4]^{2+}$. In fact, the molecular structure of **6** (Figure 2)[9] is analogous to that observed for the cationic rhodium complex **3**, but contains two additional iodine atoms bonded to the terminal metal centers. Most of the geometric descriptors are similar for both structures: staggered conformation of the dinuclear $[(CNtBu)_2Ir(\mu\text{-}pz)_2Ir(CNtBu)_2]$ moieties (131.0(3)°), parallel arrangement of the internal metal coordination planes (6.8(3)°), and an almost linear metal chain (166.56(2)°). However, the presence of the terminal iodide ligands significantly affects the metal–metal separation. Thus, while the pyrazolate-bridged Ir(1)–Ir(2) bond distance of 2.7268(7) Å is identical to the mean value in **3** (2.722(4) Å), the internal unsupported Ir–Ir separation is

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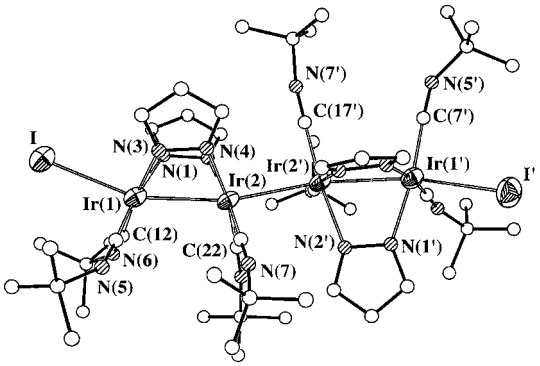


Figure 2. Molecular representation for the tetranuclear iridium complex $[\{(CNtBu)_2(I)Ir(\mu\text{-}pz)_2Ir(CNtBu)_2\}_2]$ (**6**). Only one moiety has been drawn for the disordered CN*t*Bu ligands. Selected bond lengths [Å] and angles [°]: Ir(1)–Ir(2) 2.7268(8), Ir(2)–Ir(2′) 2.8037(10), Ir(1)–I 2.8907(10), Ir(1)–N(1) 2.081(8), Ir(1)–N(3) 2.058(8), Ir(2)–N(2) 2.109(7), Ir(2)–N(4) 2.099(7), Ir–C 1.870(9)–1.896(8); Ir(1)-Ir(2)-Ir(2′) 166.57(2), I-Ir(1)-Ir(2) 159.04(3), Ir-C-N 172.1(12)–178.8(9), C-N-C 147.3(11)–170.2(12). Primed atoms are related by the symmetry transformation $2-x, y, 1/2-z$.

elongated to 2.8038(8) Å. This situation has also been reported for the closely related complex $[\{(CO)_2(I)Ir(\mu\text{-}btzt)_2Ir(CO)_2\}_2]$ (btzt = benzothiazol-2-thiolate),[10] which has a face-to-face arrangement of the coordination planes in a head-to-head configuration, with intermetallic separations of 2.731(2) Å (ligand-bridged) and 2.828(2) Å (unsupported bond).

An extended Hückel molecular orbital (EHMO) calculation[11] fully supports the proposed stabilization of the unsupported metal–metal bond, and therefore the formation of the tetranuclear blue complexes. Figure 3 shows a qualitative MO diagram of the metal–metal bonding system

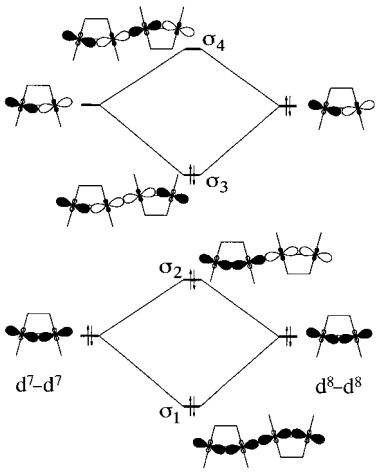


Figure 3. Qualitative fragment MO diagram for the metal–metal bonding system.

calculated from the interaction of two dinuclear $d^7-d^7$ and $d^8-d^8$ fragments, under the assumption of the geometry in **3**. Mixed-valence condensation gives rise to a fractional oxidation state for all metal centers. Partial filling of the frontier orbitals $\sigma_3$ and $\sigma_4$ appears to be essential for the stabilization of these tetranuclear complexes, as shown for the platinum blue compounds, in which these MO orbitals are fully ($\sigma_3$) and partially ($\sigma_4$) occupied.[12]

In summary, tetrametallic chains of rhodium and iridium with unsupported metal–metal bonds and fractional oxidation states, analogous to the platinum blue compounds, have been obtained. These chains are stable enough to persist in solution, and form even though the starting dinuclear complexes do not present the most favorable steric requirements for an unsupported metal–metal bond. To generate the tetranuclear chain, a noticeable deformation of the environments of the inner metal atoms must occur. This observation illustrates the greater influence of electronic over steric effects on the formation of this type of rhodium and iridium blue compounds.

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[7] a) Crystal data for **3**: $C_{52}H_{84}F_{12}N_{16}P_2Rh_4 \cdot C_4H_{10}O \cdot 0.5\,C_3H_6O$, $M_r = 1738.09$, monoclinic, $P2_1/c$ (no. 14), $a = 31.741(6)$, $b = 12.345(2)$, $c = 21.435(5)$ Å, $\beta = 96.706(16)°$, $V = 8342(3)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.384$ g cm$^{-3}$, $F(000) = 3536$, $T = 150.0(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 0.886$ mm$^{-1}$). Data collected on a Siemens P4 diffractometer on an oil-coated, rapidly cooled crystal ($0.64 \times 0.22 \times 0.14$ mm) mounted directly from the solution. Of 5404 reflections collected by $\omega$ scans ($4 \le 2\theta \le 35°$), 5186 were unique (2311 with $I \ge 2\sigma(I)$). A $\Psi$-scan absorption correction gave min./max. transmission factors of 0.79/1.00. The structure was solved by direct methods (SIR92; A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Cryst.* **1994**, *27*, 435), and refined by full-matrix least squares on $F^2$ (SHELXL-97; G. M. Sheldrick, Göttingen, **1997**). Static disorder of both $PF_6^-$ anions and of the methyl groups of two CN*t*Bu ligands was detected. The molecule disorder was modeled stepwise. Two different positions were included for each disordered moiety, which were refined with complementary occupancy factors, free displacement parameters, and some geometrical restraints. The metal, phosphorous, and four fluorine atoms were refined anisotropically. Hydrogen atoms were not included in the model. Final agreement factors were $R_1 = 0.0887$ (observed reflections) and $wR_2 = 0.2476$ (5186 reflections) for 484 parameters and 125 restraints; GOF = 0.998. Largest peak and hole in the final difference map 0.776 and $-0.621$ e A$^{-3}$. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100951.

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Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[9] Crystal data for **6**: $C_{52}H_{84}I_2Ir_4N_{16}\cdot 0.5\,C_6H_6$, $M_r = 1995.0$, monoclinic, $P2_1/c$, $a = 17.692(3)$, $b = 11.1225(13)$, $c = 20.959(3)$ Å, $\beta = 111.128(11)^\circ$, $V = 3847.1(10)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.722$ g cm$^{-3}$, $F(000) = 1886$, $T = 200.0(2)$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å, $\mu = 7.739$ mm$^{-1}$). Data collected as described above for **3** with an orange crystal ($0.30 \times 0.23 \times 0.10$ mm) in the range $4 \le 2\theta \le 50^\circ$. Of 8285 reflections, 6752 were unique. The data were corrected for absorption (Gaussian face-indexed method, SHELXTL 5.03., Siemens Analytical X-ray Instruments, Inc., Madison, WI 1994); min./max. transmission factors of 0.201/0.483; structure solution and refinement as described for **3**. After isotropic refinement, it was evident that heavy static disorder was present which affected three *tert*-butylisocyanide groups and the solvent molecule. Two different positions were included for each disordered moiety, and the refinement was carried out as described for **3**. Hydrogen atoms were only included in calculated positions for the nondisordered pyrazolate ligands. Final agreement factors were $R_1 = 0.0414$ (4270 observed reflections) and $wR_2 = 0.0964$ (all data) for 341 parameters and 68 restraints; GOF = 0.910. Largest peak in the final difference map 1.21 eA$^{-3}$ (close to Ir).[7b]

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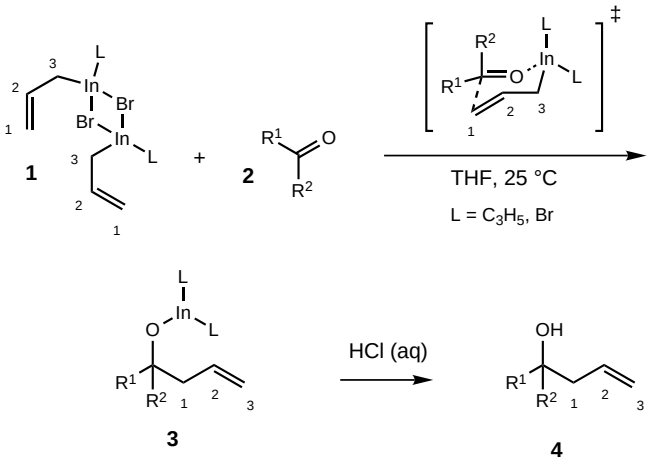
## Homoallyl-Substituted Vinylcyclopropanes from $\alpha,\beta$-Unsaturated Ketones and Allylindium Derivatives**

Henning A. Höppe, Guy C. Lloyd-Jones,* Martin Murray, Torren M. Peakman, and Kenneth E. Walsh

Organoindium species are of particular appeal as reagents for organic synthesis because they are often stable under aqueous and even mildly acidic conditions and are compatible with many organic functional groups.[1] Allylindium sesquihalides $(allyl)_3In_2X_3$ and dihalides $(allyl)_2In_2X_4$ **1**, prepared by the reaction of allyl halides with indium metal[2] or indium halides,[3] react smoothly with aldehydes and ketones[4] **2** via transition states of the Zimmermann–Traxler type to afford indium alkoxide intermediates **3** (Scheme 1). Hydrolysis yields homoallylic alcohols **4**.[5] Here we report on the




Scheme 1. Reaction of allylindium sesquibromide **1** with ketones **2** to give **3** and **4** via a Zimmerman–Traxler transition state.

reaction of **1** with $\alpha,\beta$-unsaturated ketones or aldehydes **5** to produce homoallylic indium alkoxide intermediates **6**, which can be induced to undergo a deoxygenative rearrangement that results in vinylcyclopropane derivatives of type **7** (Scheme 2).

In initial experiments, dibenzylideneacetone **5a** was allowed to react under nitrogen with freshly prepared $(C_3H_5)_3In_2Br_3$ (**1**) in anhydrous THF at 25 °C (**5a**:In = 1:1). After the mixture was diluted with $Et_2O$, worked up with 1M HCl, and subjected to column chromatography, we obtained analytically pure **7a** in yields of 40–60 %.[6] Thus, a reaction took place that did not lead to **8a**, but instead resulted in cleavage of the C–O bond. Presumably this involved coupling between the allylindium moiety (C(4)–C(6)) in **6a** and the C(3) terminus of the initially transferred allyl group (C(1)–C(3)) to afford the homoallyl-substituted vinylcyclopropane derivative **7a**. The overall reaction therefore involves deoxygenative sequential transfer of six carbon atoms (two allyl moieties) from the indium sesquihalide species **1** to the $\alpha,\beta$-unsaturated ketone **5a**. A three-membered ring is formed by linkage of the carbonyl carbon atom with C(1) and C(2) of the first allyl unit. After many experiments it became clear that removal of the THF[7] (which presumably stabilizes the intermediate) and exposure of the crude product to air in an acidic medium[8] (which may induce homolysis of the C–In bond, possibly by insertion of $O_2$) is essential for efficient and reproducible diversion of **6** to **7** rather than to **8**.

We suspected that rearrangement of **6** to **7** might involve the reaction of $CH_2{=}CHCH_2In(L)_x$ with aerobic oxygen to afford an intermediate of the type $CH_2{=}CHCH_2(O)_nIn(L)_x$ ($n = 1,2$). The following experiments were performed to circumvent the requirement of exposure to air. One equivalent of $(C_3H_5)_2In_2I_4$, in which each indium atom bears only one allyl group, was allowed to react with **5a** (THF, 25 °C,

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